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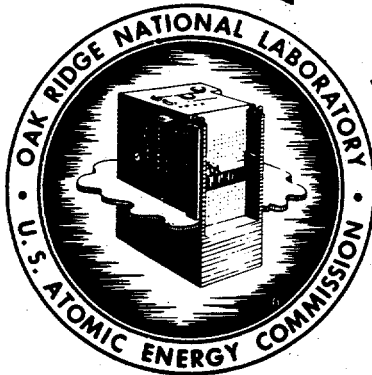
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THE DISPOSAL OF POWER REACTOR  
WASTE INTO DEEP WELLS



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Wallace de Laguna and J. O. Blomeke

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## THE DISPOSAL OF POWER REACTOR WASTE INTO DEEP WELLS

Wallace de Laguna and J. O. Blomeke

For various reasons it is not possible to leave the uranium or other nuclear fuel in a power reactor until all of it has been "burned up" by fission. In the case of liquid fuel (homogeneous) reactors a small part is continuously bled out, purified and returned. In the case of solid fuel reactors, fuel elements are periodically removed, reprocessed and the "unburned" fuel put back into service. In both cases the purification produces wastes which contain radioactive fission products and transuranic elements, and it is with the disposal of these wastes that we are concerned. For technical reasons we will limit our consideration to the wastes from the processing of solid fuel elements, and from the processing of the very similar solid "blanket" elements in which fissionable fuel is made from non-fissionable isotopes of uranium and thorium by interaction with neutrons in the outer regions of the nuclear reactor.

Although they constitute the hazard, the fission products, their stable end products, and the transuranic elements make only a negligible contribution to the gross chemical composition of the wastes. This chemical composition is determined by the nature of the fuel elements, which must contain far more than just the uranium or other fissionable fuel, and by the particular method of chemical separation that is used to process the fuel elements after they have been removed from the reactor.

For the purposes of this brief summary, the many possible types of fuel elements will first be divided into those containing essentially the natural proportion of  $U^{235}$  and  $U^{238}$ , and those in which the proportion of  $U^{235}$  has been very substantially increased.

The natural uranium fuel slugs are for the most part cylinders an inch or so in diameter and anywhere from several inches to several feet in length. The uranium is very carefully clad with an aluminum jacket, not only to retain the fission products, which would otherwise contaminate the water or air used for cooling, but also to prevent the coolant from reacting chemically with the hot uranium metal and to provide mechanical strength. After the fuel element is removed from the reactor, the first processing step is to remove the aluminum jacket. This may be done either by stripping it off mechanically or by dissolving it chemically. The aluminum metal or the sodium aluminate solution contains a small amount of fission products, which diffused into the jacket from the fuel. The mechanically removed jackets, not being particularly soluble, could be disposed of into pits or trenches, later filled and then covered with a thin impermeable blanket membrane to deflect the rain. If caustic is used, the sodium aluminate solution is generally added to the main waste streams; but for disposal into deep wells, this may not be desirable.

Many processes are under consideration; but in the one important to us, after dejacketing, the uranium core is dissolved in nitric acid and this solution passed counter-currently through a stream of organic solvent, which removes the uranium and the newly created fissionable plutonium, while leaving the fission products behind in the aqueous phase. Two similar but distinct processes are used.

"Redox", the older of the two processes, uses hexone as the organic solvent. In order to drive the fuel into the solvent while keeping the fission products back, it is necessary to salt the aqueous phase with large quantities of aluminum nitrate. The waste is therefore dominantly acid aluminum nitrate. The fresh waste, containing many short-lived rapidly decaying fission products, is intensely radioactive and to facilitate the final disposal, it is stored in tanks to age. To reduce the corrosiveness of the waste, and so prolong the life of the tanks, the waste is neutralized with sodium hydroxide. This reacts with the aluminum nitrate to form sodium aluminate, which decomposes on standing, forming precipitates and sludges that settle to the bottom of the tank. Sodium nitrate is also formed; this largely remains in solution. To prepare waste such as this for disposal into a deep well it would have to be aged, centrifuged, and filtered to remove the aluminum and other insoluble hydrates and hydroxides, and diluted to reduce the viscosity, to prevent precipitation of sodium nitrate, and to reduce the problems of overheating after disposal. In these respects, the treatment would be much the same as for any of the wastes, but it would be made somewhat more difficult, because of the need to remove substantial amounts of aluminum hydroxide, which is hard to handle. On the other hand, this precipitate would entrain a substantial part of the fission products which, now in solid form, could be stored safely at the surface, thus reducing the thermal problems of disposing of the liquid phase into the ground.

The "Redox" method of separation was so named because reduction and oxidation are used to separate the plutonium and uranium. It has now largely given way to "Purex", a name which stands for "plutonium-uranium extraction". The de jacketing and primary solution in nitric acid are much the same for both methods; the difference comes in the choice of organic solvent. Purex uses tributyl phosphate, referred to as TBP. This solvent acts differently from hexone; it must be diluted with a hydrocarbon such as kerosene, and nitric acid is used as the salting agent to force the separation (not aluminum nitrate). The waste is, therefore, very largely a solution of the fission products in nitric acid together with a little iron and other material picked up by corrosion. Because it is relatively low in dissolved solids, it can be greatly reduced in volume by evaporation. There is, however, a catch. Very small amounts of TBP are left in the aqueous waste stream and when heated in the evaporator may react with the nitric acid and explode. In some cases, this unpleasant eventuality is eliminated by carefully stripping all the TBP, in others by neutralizing the waste with sodium hydroxide before evaporation.

As these wastes are aged, a precipitate (predominately sodium nitrate) is formed, occupying about 10% of the waste volumes. This granular precipitate is much easier to handle than the flocculent precipitate formed by aluminum hydroxide, and it would not be difficult to pump both supernatant and precipitate out of the tank, separate them by centrifuging and filtration, and return the solids to the tanks. The clear liquid could, after dilution, be disposed of into deep wells. It would carry with it a larger proportion of the fission products than would be the case with the liquid resulting from "Redox" separation, for the Purex sludge carries with it a smaller proportion of fission products than does Redox sludge.

The natural uranium fueled reactors are poorly adapted to breeding or to the economical production of commercial power. The enriched fuel reactors, with  $U^{238}$  or thorium blankets for breeding, will probably be the major power sources of the future. Three general types of fuel elements are being considered for these reactors, differing in the choice of metal used to alloy with or clad the fissionable material. The first type is the aluminum-alloy, aluminum-clad element. This differs from the natural uranium element described above in its shape and fabrication and in that the core of the element is an alloy of uranium and aluminum, not pure uranium metal, and which preclude mechanical dejacketing. The whole element must therefore be dissolved giving a solution rich in aluminum nitrate. In the "25" process, this is treated with hexone as in the Redox process, and the waste is similar to the Redox waste. Salting with aluminum nitrate is not necessary for the fuel elements contain over 90% aluminum. The uranium-aluminum alloy fuel elements are not at present regarded as potentially the most useful for power reactors; stainless steel and zirconium elements appear to hold greater promise.

For the stainless steel elements, a process called Darex -- for dilute aqua regia extraction -- is under development. The fuel would be dissolved in a mixture of hydrochloric and nitric acids, an obvious problem being the manufacture of the vessels in which this dissolution could take place. The resulting solution would then be stripped of the hydrogen chloride, for this is what makes the solution so very corrosive, although it is unlikely that all traces can be removed. The unburned fuel is then separated from the nitric acid solution with TBP, giving a waste somewhat similar to that from the "Purex" process. There will be, however, much iron, chromium, and nickel present, although far less than the Redox waste. These can be separated without serious trouble, and will carry many of the fission products with them, although not the cesium-137. If traces



of chloride do remain in the waste, it may be more corrosive and harder to store than that from the true "Purex" process, and consequently, it may be desirable to dispose of it without decay storage.

There are two processes under consideration for treating the uranium-zirconium fuel elements. The first, called FAN--for fluoride and aluminum nitrate, begins with dissolution of the fuel elements in a mixture of hydrofluoric acid, nitric acid, and aluminum nitrate. The amount of fluoride needed depends upon the proportion of zirconium in the fuel, which differs considerably from one type of fuel element to another. The amount of aluminum nitrate is appreciably less than is used in the "Redox" process. The solution is treated with TBP to remove the unburned fuel. The waste is in a sense intermediate between Redox and Purex in that it has an intermediate amount of aluminum nitrate. It differs from these however in that the fluoride makes it very corrosive and difficult to store, more difficult in general than the Darex wastes. It is hard to predict what effect the presence of the zirconium will have. In neutral solutions, it tends to complex with the fluoride, in which form it stays in solution, and might not interfere with disposal into deep wells. The complexes break down, however, at the high pH at which these solutions are stored, and also break down as the result of radiation damage, and the resulting zirconium hydroxide precipitate is hard to separate. The FAN wastes might turn out to be the most difficult to dispose of into deep wells.

Another process under development for handling zirconium alloy fuel elements is called "Zircex". The fuel elements may be prepared for this process by mechanically chopping them into small pieces to increase surface area. These small solid pieces are treated then with hydrogen chloride gas to form zirconium chloride which is volatile and can be driven off by heating. Once freed of the zirconium, the remaining uranium is dissolved in nitric acid and then separated

from the fission products with TBP. This produces a typical Purex-type waste, which may contain traces of chloride making it harder to store.

The blankets from the breeder reactors, that is, the fertile uranium-238 and thorium-232, which is being converted into fissionable fuel, will have to be reprocessed in much the same fashion as the spent fuel elements. Two general types of breeder reactors are being considered--thermal and fast--depending on the average speed of the neutrons used to produce fission. For the fast breeders, uranium-238 forms the best blanket material and will presumably be used in elements much like the fuel elements themselves. These can be processed by one of the methods described above. The wastes will, therefore, be chemically similar to the corresponding fuel processing wastes, but the level of activity will be lower.

For thermal breeders, thorium forms the better blanket material. Thorium-232 is not transformed directly into fuel, but is transmuted by neutron capture into thorium-233, which decays to protactinium-233, which in turn decays with a half-life of 27.4 days to uranium-233, the desired product. When the thorium blanket is processed, it is necessary to save both the  $U^{233}$  and the  $Pa^{233}$ . For this, the Thorex process is used. The thorium is dissolved in nitric acid with catalysis by fluoride ion. The thorium,  $U^{233}$  and  $Pa^{233}$  are extracted and separated from fission products by use of a TBP solvent extraction process. It is necessary to salt the aqueous phase with aluminum nitrate. The waste is therefore much like Redox waste, except that the fission product activity level is lower.

The Sulfex process (for sulfuric acid, extraction) is one of a number of processes which are in as yet a preliminary stage of development. These processes propose to dissolve stainless steel-clad fuels or zirconium-clad fuels or alloys in sulfuric acid. The effluent waste streams will undoubtedly contain significant

amounts of sulfate, and possibly dissolved stainless steel or zirconium.

Separation and recovery of uranium and plutonium will be effected by extraction with TBP.

The following generalizations may be made, if the reader will remember that the actual operations are far more complex than we can cover here.

Present wastes are all nitrate solutions, and may contain appreciable sodium nitrate resulting from the neutralization of nitric acid with sodium hydroxide. They also contain (if neutralized) either aluminum hydroxide, zirconium hydroxide, or a mixture of iron, nickel and chromium hydroxides, depending on the type of fuel element. The amount of these hydroxides varies greatly between the various waste types. It appears probable that all of the wastes will be aged in tanks before ultimate disposal, to permit the decay of the shorter-lived fission products. This aging may have to be cut short for those wastes which are particularly corrosive because of the chloride or fluoride which they contain.

If the aged wastes are to be disposed of into a deep well, they will have to be centrifuged and filtered to remove precipitates and suspended solids. There is equipment which will do this. These solids will carry with them a part of the activity, and, in the case of some of the wastes, a large part. This solid material will have to be disposed of at the surface. This is not necessarily a disadvantage, for if untreated waste could be put directly down a well, formidable problems would result from the subsequent generation of heat. Indeed, it may be desirable to treat some of the more concentrated types of waste, like Purex, to remove a part of the activity.

The question might then be asked, if a large part of the activity must be removed from the waste solutions and stored in some fashion at the surface, why not continue the treatment--remove all of the fission products and transmutation

Process	Fuel Type	Chemical Composition of Concentrated Unneutralized H <sub>1</sub> -level Wastes	Volume gal/ton U	Chemical Composition of Concentrated, Neutralized Wastes	Volume gal/ton U
Purex	Normal or slightly Enriched U	7 M HNO <sub>3</sub> Traces: Fe, Ni, Cr, U, Hg	120 120	0.41 M NaAlO <sub>2</sub> 0.37 M NaOH 1.44 M NaNO <sub>3</sub> 0.31 M NaNO <sub>2</sub> 0.023 M Fe(OH) <sub>3</sub> Traces: Na <sub>2</sub> SiO <sub>3</sub> , Hg Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> , Na <sub>2</sub> SO <sub>4</sub>	765
Redox	Normal U, Aluminum-clad	65.4 wt% ANN (Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O) 4.9 wt% NaNO <sub>3</sub> ~1.2 M HNO <sub>3</sub>	1200	7.4 wt% NaAlO <sub>2</sub> 4.4 wt% NaOH 25.7 wt% NaNO <sub>3</sub> Traces: Fe, Ni, Cr, U, Si, Hg	2600
Thorex	Thorium-U <sup>233</sup>	0.55 M Al <sup>+</sup> <sub>3</sub> ~0.11 M HNO <sub>3</sub> ~0.03 M F <sup>-</sup> Traces: Fe, Ni, Cr, Hg, Po <sub>4</sub> , SO <sub>4</sub> , Si	1400	~0.4M HNO <sub>3</sub> 2.0 M Al <sup>+</sup> <sub>3</sub> ~0.1 M F <sup>-</sup> Traces: Fe, Ni, Cr, Si, Po <sub>4</sub> , SO <sub>4</sub> , Hg	400
Darex	Stainless Steel Clad slightly enriched U metal or oxide	2.3 M HNO <sub>3</sub> 20-80 g/liter dissolved Si Traces: Fe, Ni, Cr, Cl	1200	Not neutralized	-
FAN	Zirconium clad, Zr-U alloy	3.5-7 M HNO <sub>3</sub> 0.2-1.6 M Al <sup>+</sup> <sub>3</sub> 0.2-1.1 M F <sup>-</sup> 0.03-0.2 M Zr <sup>+</sup> <sub>4</sub> 4-11 M HNO <sub>3</sub>	3000	Not neutralized	-
Sulfex	Stainless Steel or Zr Clad	7 M HNO <sub>3</sub> 2.5 M H <sub>2</sub> SO <sub>4</sub> 10-40 g stainless steel Traces: Fe, Ni, Cr, etc.	2300	Not neutralized	-

products from the waste, and discharge a harmless liquid to the nearest stream? The answer is the very high decontamination factor that would be required to make the waste harmless. Satisfactory treatment would require the removal, not of 99 per cent, or 99.99 per cent, but of all but one part in many billions or hundreds or thousands of billions, for the long-lived fission products are poisons quite in a class by themselves.

Even after nuclear power has grown to an important place in our economy, it is anticipated that there will be only a very few--possibly only three--fuel-and-blanket element processing plants to which spent elements will be sent from many widely scattered reactors. This is because the processing plants must be heavily shielded and the equipment operated, repaired, and replaced by remote control, which is expensive. A single plant, with all its accessory equipment, may well cost the better part of a billion dollars and would be designed to use not only one, but several of the processing methods described above.

The solid fuel elements can be shipped with relative safety, but to ship liquid radioactive wastes would create such a hazard, in case of an accident, that waste disposal had better be at the plant site. This means a site suitable for the disposal of many kinds of wastes: solid, liquid, and gaseous. Two types of disposal--and therefore two types of sites--are being seriously considered: salt and deep wells

#### Disposal into Salt Formations

The successful storage of petroleum products in cavities dissolved out of salt shows that such cavities can be made cheaply and to the dimensions specified, that they do not leak, and that they are strong. They would make excellent storage vessels for the radioactive wastes were it not for the heat generated by the wastes. Artificial cooling would be difficult, because the combination of nitrate and chloride ions is so very corrosive. Natural cooling by conduction through the